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HIGH-TEMPERATURE AND LATE HYDROUS Ca-MINERALS IN THE THERMALLY METAMORPHOSED LIMESTONE XENOLITHS FROM THE BASALT OF RACOSU DE JOS, PERSANI MTS. (ROMANIA)

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Introduction

There is a well-known basalt area in the Persani Mts., famous for upper mantle-derived xenoliths, consisting of olivine and pyroxenes (Downes et al., 1995). There are also different xenoliths of lithospheric origin, such as: conglomerates, sandstones, clays, marls, limestones, marbles, and possibly dolomites. Quartz xenoliths, contact metamorphic minerals that have been formed at the contact of xenoliths and the enclosing basaltic melt were described by Maldarescu et al. (1982). Carbonate-containing xenoliths were mentioned and examined by Marza et al. (1994). He determined high-temperature Ca-silicate assemblages with gehlenite, larnite, wollastonite, together with tridymite, quartz, feldspars and diopside in the microskarn environments. Szakáll *et. al.* (2006) mentioned levyne, ettringite and okenite for the first time from Neogene basalts of the Persani Mts.

Samples and methods

The different xenolith types were collected recently from the basalt quarries near Racosu de Jos. The presence of euhedral crystals of few minerals in the cavities is a general characteristic of all samples. The host rock has a polycrystalline, polymineralic matrix. Samples were prepared under stereomicroscope to be able to perform pure samples for the measurements. X-ray powder diffraction (XRPD) phase identification was carried out at the Department of Mineralogy and Petrology, University of Miskolc, completed with Scanning Electron Microscopy (SEM) observations and Energy Dispersive Spectrometry (EDS) at the Department of Metallurgy, University of Miskolc. XRPD patterns of samples were resolved by search/match operation and full profile matching (FPM) by pseudo-Voight fitting algorithm with the EVA-Diffracplus evaluation software of Bruker. Detailed chemical

analyses (EPMA) were performed at the Department of Earthsciences, University of Modena Reggio Emilia.

Results

The identified minerals of the thermally metamorphosed carbonaceous (mainly Ca carbonates) xenoliths, are similar to a skarnification process. Two different mineral groups were classified on their relative temperature of crystallization (Table 1), a High- and a Low-temperature one. The matrix of the xenoliths is build up by high temperature Ca-silicate

Table 1. Genetic classification of identified Ca containing phases

Type of matrix	High temperature Ca mineral associations	Low temperature hydrated Ca mineral associations
I	wollastonite	thaumasite, erionite
II	larnite, andradite and brownmillerite	afwillite, thaumasite, tobermorite
III	gehlenite, diopside, andradite	ettringite, chabazite, levyne, okenite, plombierite

associations. On the basis of mineralogical composition, three types of associations were identified:

Type I. The xenolithe has a wollastonite matrix, with euhedral, mm-sized hexagonal prismatic thaumasite crystals (Table 2., AR_2b).

Sample	#046-1360		AR 2b		AR-B 1a	
Lines	d(Å)	I(%)	d(Å)	I(%)	d(Å)	I(%)
(100)	9.590	100	9.593	100	9.593	100
(112)	3.801	23	3.798	22	3.799	23
(110)	5.530	22	5.532	21	5.527	27
(123)	2.511	16	2.510	14	o.l	
(121)	3.423	14	3.421	12	3.421	12
(302)	2.726	14	2.724	12	o.l	
(223)	2.166	13	2.165	11	2.165	13
(111)	4.892	12	4.887	11	4.890	11
R/R0			1.76		1.95	
RWP %			15.8		13.5	

Table 2. Results of XRPD analyses for thaumasite, compared to the #046-1360 PDF pattern. Some overlapping (o.l.) of the reflections by accompanying phases occur. (R_{wp} weighted reliability of FPM fitting, $R=R_{wp}$, $R0$ discrepancy)

Tpe II. This type has an andradite, larnite and brownmillerite (and babingtonite) matrix (Fig.1.) According to Shmulovich (1967) the stability of larnite in the CaO-SiO₂-CO₂ system is situated over 800 °C, for the spurrite + wollastonite = larnite + CO₂ transformation reaction. Tobermorite (and possibly rapidcreeckite) occur as white earthy nests and crusts in the brownish, dark grey matrix. Euhedral, colourless, 1-3 mm-sized, lath-like or tabular

crystals of afwillite (Table 3., ARB_1b) and thaumasite are developed in vugs of the matrix. A similar association was described by Jasmund and Hentschel (1964) from the Eifel Mts.,

Germany.

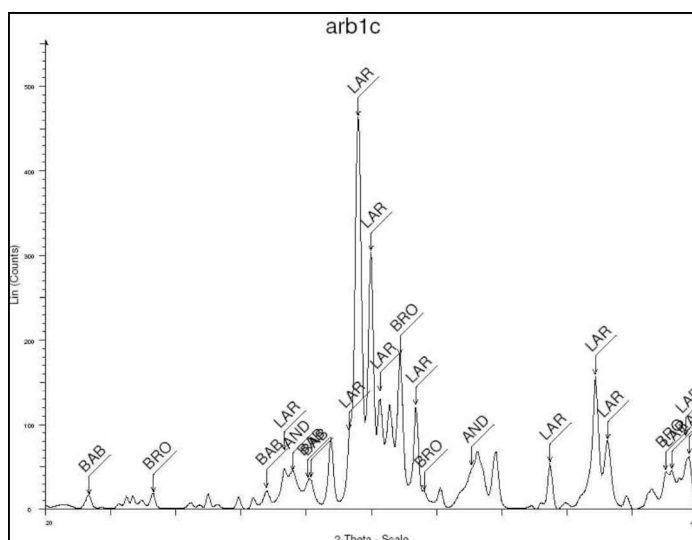


Fig.1. FPM fitted XRPD pattern of the matrix of type II xenolith. (LAR-larnite, BAB-babingtonite, BRO-brownmillerite, AND-andradite) (Cu, $\lambda=1.5406$, 40 kV, 40 mA).

Sample	#070-0014		AR-B 1b		AR-J 1b	
Lines	d(Å)	I(%)	d(Å)	I(%)	d(Å)	I(%)
(310)	3.175	100	3.173	97	3.173	93
(-314)	2.834	89	2.833	99	2.833	100
(-512)	2.727	84	2.726	77	2.727	83
(-202)	6.543	52	6.541	56	6.541	54
(020)	2.816	49	2.816	100	2.816	100
(110)	5.061	27	5.060	31	5.060	31
(-404)	3.272	26	3.270	26	3.270	25
R/R0			3.76		4.19	
RWP %			21.3		25.4	

Table 3. Results of XRPD analyses for afwillite, compared to the #070-0014 PDF pattern. Some overlapping (o.l.) of the reflections by accompanying phases occur. (R_{wp} weighted reliability of FPM fitting, $R=R_{wp}$, R0 discrepancy)

Type III. A gehlenite, diopside, andradite association was determined in the third type of matrix, with small amount of tobermorite. For this type, the presence of ettringite (Table 4, G218), chabazite (1-2 mm rhombohedrons) and levyne (1-2 mm tabular crystals) was confirmed. Plombierite (blue-white, glass-like crusts sometimes with globular surfaces) and okenite (and possibly para-alumohydrocalcite) were identified by XRPD and optical microscopy observations.

Sample	#041-1451		G218		G187-2	
Lines	d(Å)	I%	d(Å)	I%	d(Å)	I%
(100)	9.720	100	9.737	100	9.738	100
(110)	5.610	76	5.607	89	5.604	94
(114)	3.873	31	3.877	37	3.880	40
(216)	2.560	29	2.56	30	2.561	35
(212)	3.475	23	3.475	22	3.475	24
(226)	2.206	22	2.205	26	o.l.	

Table 4. Results of XRPD analyses for ettringite compared to the #041-1451 PDF pattern. (R_{wp} weighted reliability of FPM fitting, $R=R_{wp}$, R0 discrepancy)

The low-temperature minerals may have formed by hydrothermal processes, which affected the primary high-temperature minerals of the matrix, thus they occur in the cavities and fissures of the xenoliths. Gross (1977) mentioned a temperature of 110 °C for the formation of tobermorite, afwillite etc. by autoclaving. According to this assumption, wollastonite may have altered to thaumasite (SO₄ substitution by CO₃ identified by EDS), while alteration of the larnite-andradite-brownmillerite assemblage give rise to afwillite, thaumasite/ettringite, hydrocalumite, tobermorite (and possibly rapidcreekite). The last products are vaterite and calcite. The gehlenite-diopside-andradite assemblage could have altered to tobermorite and plombierite, ettringite/thaumasite, levyne, erionite, and chabazite. Plombierite occur in blue-white, glass-like crusts, sometimes with globular surfaces. The late-stage minerals are calcite, aragonite, vaterite and smectite.

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